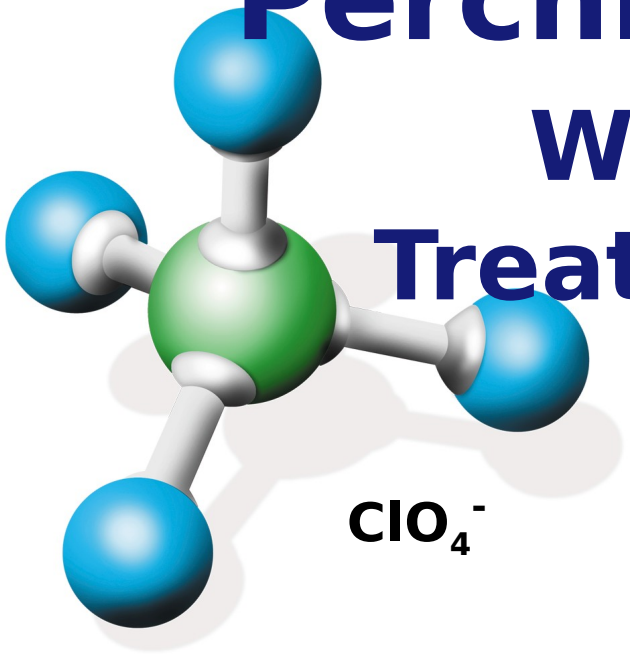
# Perchlorate Overview

## With an Emphasis on Treatment Technologies



$ClO_4^-$

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# Overview

- **Introduction –** What is perchlorate?
- **Analytical –** How do you analyze for it?
- **Toxicology –** What are the toxicological issues?
- **Regulatory History –** How did we get to this point?
- **Regulatory Timeline –** Where are we going?
- **Treatment Technologies –** How is it treated?
- **Looking to the Future** – What is needed?

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# What is perchlorate?

- **Uses of perchlorate compounds: medical treatment, rocket motors, mines, torpedoes, munitions, etc.**
- **Perchlorate ($ClO_4^-$) Chemistry**
  - Highly oxidizing salt
  - Kinetically very stable, i.e., un-reactive (especially in water)
- **What does this mean?**
  - Mobile in subsurface but stable: <u>BIG PLUMES!</u>
  - Same for surface water: <u>LARGE AREA AFFECTED!</u>
  - Treatability (*e.g.*, ex situ, in situ, physical, chemical, biological, phyto)

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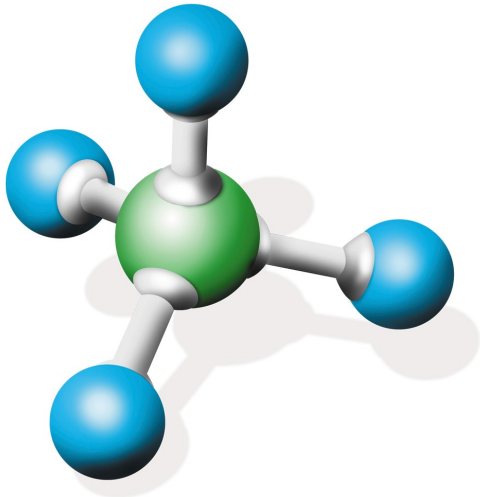
# How do you analyze for it?

- **Reporting limits: Jan 1997 – 400 ppb; Apr 1997 – 4 ppb**
- **Water (drinking and ground) US EPA Method 314**
  - Total dissolved solids (TDS)
  - Requires each lab conducting analysis to establish and verify MRL for every analysis batch
- **More Difficult Matrices**
  - Solids (fertilizer and soil)
  - Serum (rat and human)
  - Urine (rat and human)
  - Tissues (rat)
  - Milk (rat)



- **HOWEVER, there are promising analytical methods on the horizon**

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# What are the toxicological issues?

- **$ClO_4^-$ interferes with iodide uptake into the thyroid gland, therefore disrupting thyroid functions**
  - Adults – thyroid helps to regulate metabolism
  - Children – thyroid plays major role in proper development in addition to metabolism
  - Impaired thyroid function in expectant mothers may impact fetus and newborn
  - Changes in thyroid hormone levels may also result in thyroid gland tumors *in laboratory rats*
- **EPA's draft analysis of $ClO_4^-$ toxicity is that disruption of iodide uptake is key event leading to changes in development or tumor formation**

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# How did we get to this point?

- **Original EPA “standards”: 4-18 ppb (in 1992) to 18 ppb (in 1995) due to scientific uncertainties**
- **1997 – CA begins monitoring of drinking water sources**
  - Feb 02 – In 11% public water systems, 6.5% drinking water sources
- **1998 – EPA SDWA Contaminant Candidate List**
- **1999 Feb – EPA External Peer Review**
  - Resulted in proposed 32 ppb; identified additional data needs
- **1999 – Unregulated Contaminant Monitoring Rule**
  - Large drinking water providers required to monitor in 2001
- **2000 – Some states begin process of drinking water standards**

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# And then what happened?

- **2001 – EPA Regions and States begin to set low ALs**
- **2002 – States begin to request DOD facilities to sample**
  - McAlester AAP, Red River, etc.
- **2002 Mar – Peer Review Meeting**
  - EPA's second External Peer Review Panel – potential MCL of 1 ppb or lower (DOD provided comments)
- **2002 Jun – Final report from Peer Review Panel**
- **2003 Jan – US EPA reconfirms 1999 guidance of using 4 - 18ppb until RfD is finalized**

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# *Where are we going?*

- **DOD (USAF lead) to continue partnering with regulators to address lingering scientific uncertainties**
- **US EPA writing revised draft document based on Peer Review report**
- **RfD expected to be listed on IRIS by CY03**
- **2004 to 2006 – EPA sets MCL for perchlorate**

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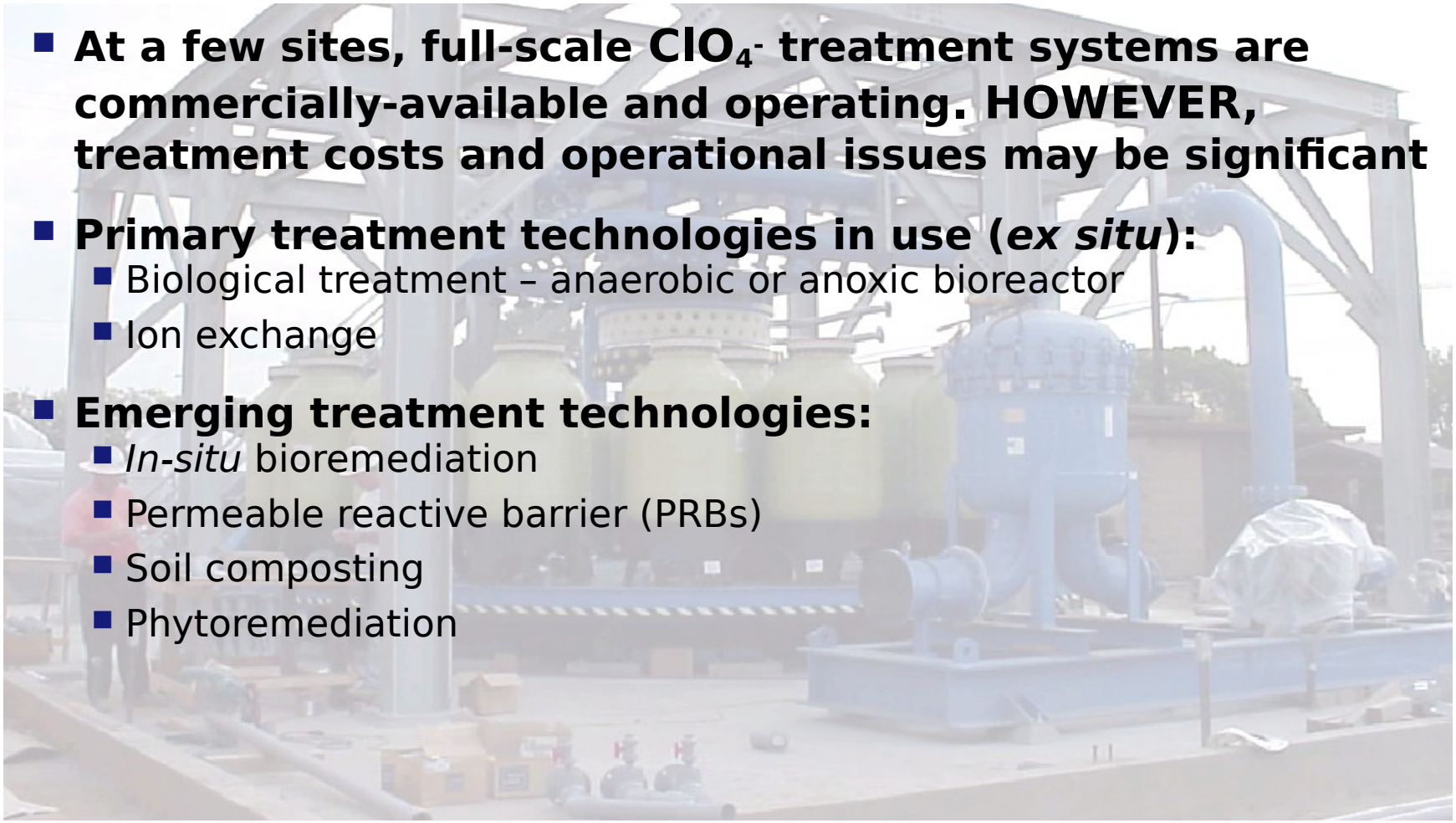
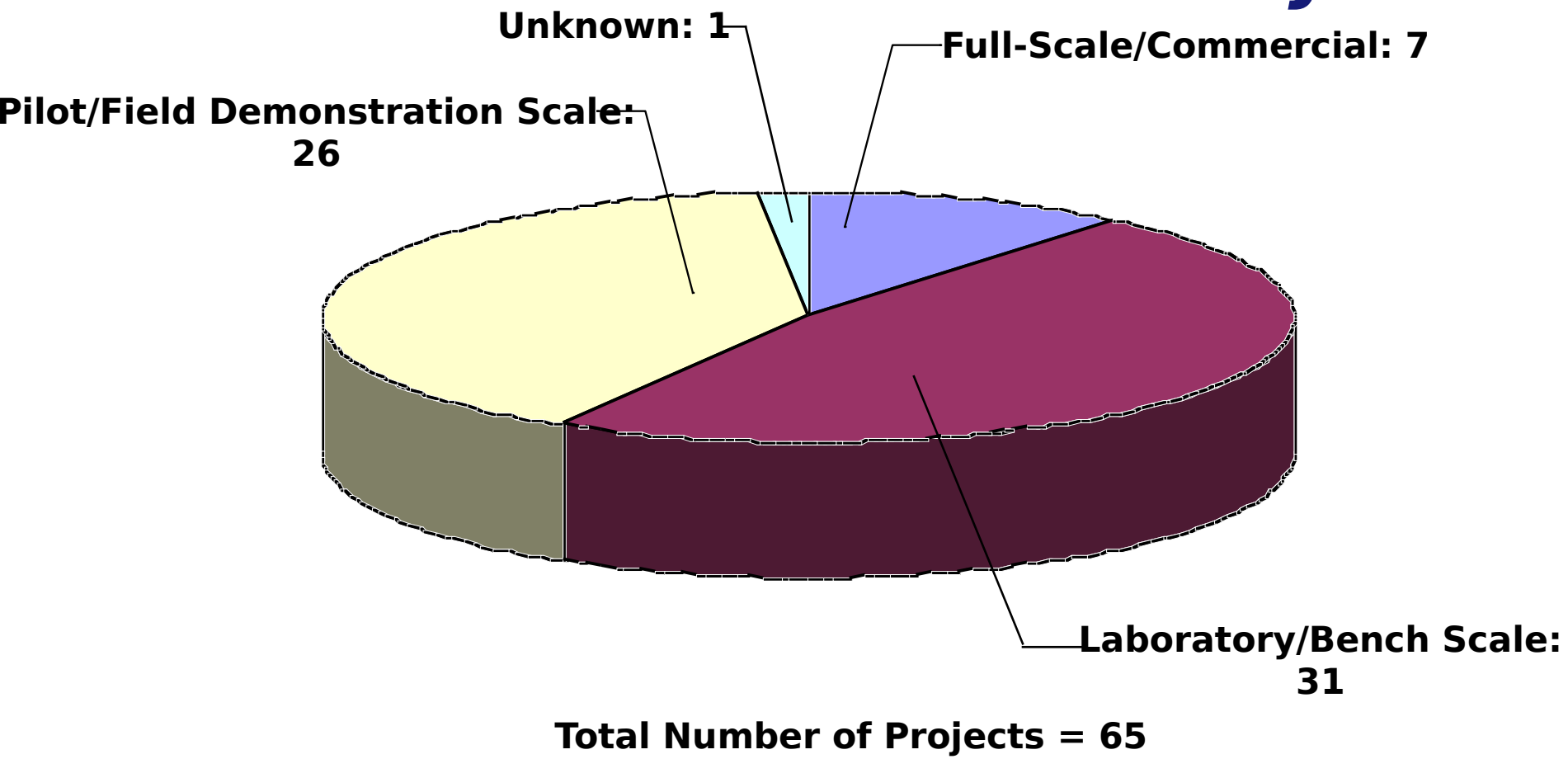
# How is it treated?



- **At a few sites, full-scale $ClO_4^-$ treatment systems are commercially-available and operating. HOWEVER, treatment costs and operational issues may be significant**
- **Primary treatment technologies in use (*ex situ*):**
  - Biological treatment – anaerobic or anoxic bioreactor
  - Ion exchange
- **Emerging treatment technologies:**
  - *In-situ* bioremediation
  - Permeable reactive barrier (PRBs)
  - Soil composting
  - Phytoremediation

# Scale of Perchlorate Treatment Technology Projects




**Total Number of Projects = 65**

As of Oct 2001

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# Example Perchlorate R&D and Commercial Relationships

## Treatment Technology Investment

- AWWRF (Mgmt. Funding)
  - Several academic institutions
  - Water purveyors
  - Municipalities
  - Federal entities
- SERDP/ESTCP (Funding)
  - Academic institutions
  - Commercial industry
- National Science Foundation
  - Academic institutions
- San Gabriel Basin Initiative

## Partnering Initiatives

- DOD
  - DOD Perchlorate Working Group (PWG)
- Industry
  - Perchlorate Study Group (PSG)
- US EPA
  - Interagency Perchlorate Steering Committee (IPSC)

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# DOD Investment

**Investment in perchlorate treatment technologies to date:**

- **Examples (Total $24M alone)**
  - **US Navy: $10.5M**
  - **US Air Force (AFRL- associated): $6.8M**
  - **US Air Force (Edwards AFB): $1.4M**
  - **US Air Force (AFRL): $0.2M**
  - **SERDP/ESTCP (OSD): $3.9M**
  - **US Army (LHAAP, *ex situ* alone): $1.2M**

As of Jan 2002

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# SERDP/ ESTCP Efforts

- **Overview of SERDP bioremediation projects (SIU, Envirogen, and Geosyntec)**
  - Biological and physico-chemical technologies
  - *Ex situ* and *in situ*
  - All concentration ranges
  - Water treatment emphasized, not much attention to soil
  - Perchlorate-degrading microorganisms are ubiquitous
- **General observations**
  - Site-specific electron donor
  - Microcosms degraded perchlorate < 30 days
  - pH lower than 6 may be a problem
  - Field tests just beginning

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# What do we know right now?

- **Chemical treatment** (e.g. Ti(III), $Fe^0$-UV, $O_3$-Perox)**:**
  - Not mature technology
  - Costly
  - More research could prove fruitful
- **Physical treatment** (*e.g.*, ion exchange, membranes)**:**
  - Mature technologies, applicable for drinking water
  - High capital and O&M costs
  - Looking for ways to optimize
- **Biological treatment** (*e.g.*, bioreactors, *in situ* bioremediation)**:**
  - Mature *ex situ*, less mature *in situ*
  - Varied cost scenarios
  - Need more data to understand bioprocesses
  - Much accomplished, many more opportunities….

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# Primary Treatment Technology: Biological Treatment

- **Basic premise: *ex situ* aboveground treatment via bioreactors**
- **Development scale: both pilot-and full-scale implementation**
- **Advantages:**
  - Relatively small, compact design
  - Easily inserted as add-on device into existing treatment syste
  - Currently available
- **Disadvantages:**
  - Long-term pump and treat technology
  - Requires careful control of reactor vessel environmental conditions
  - Treated water may still be regulated, not suitable for drinking, may require additional treatment

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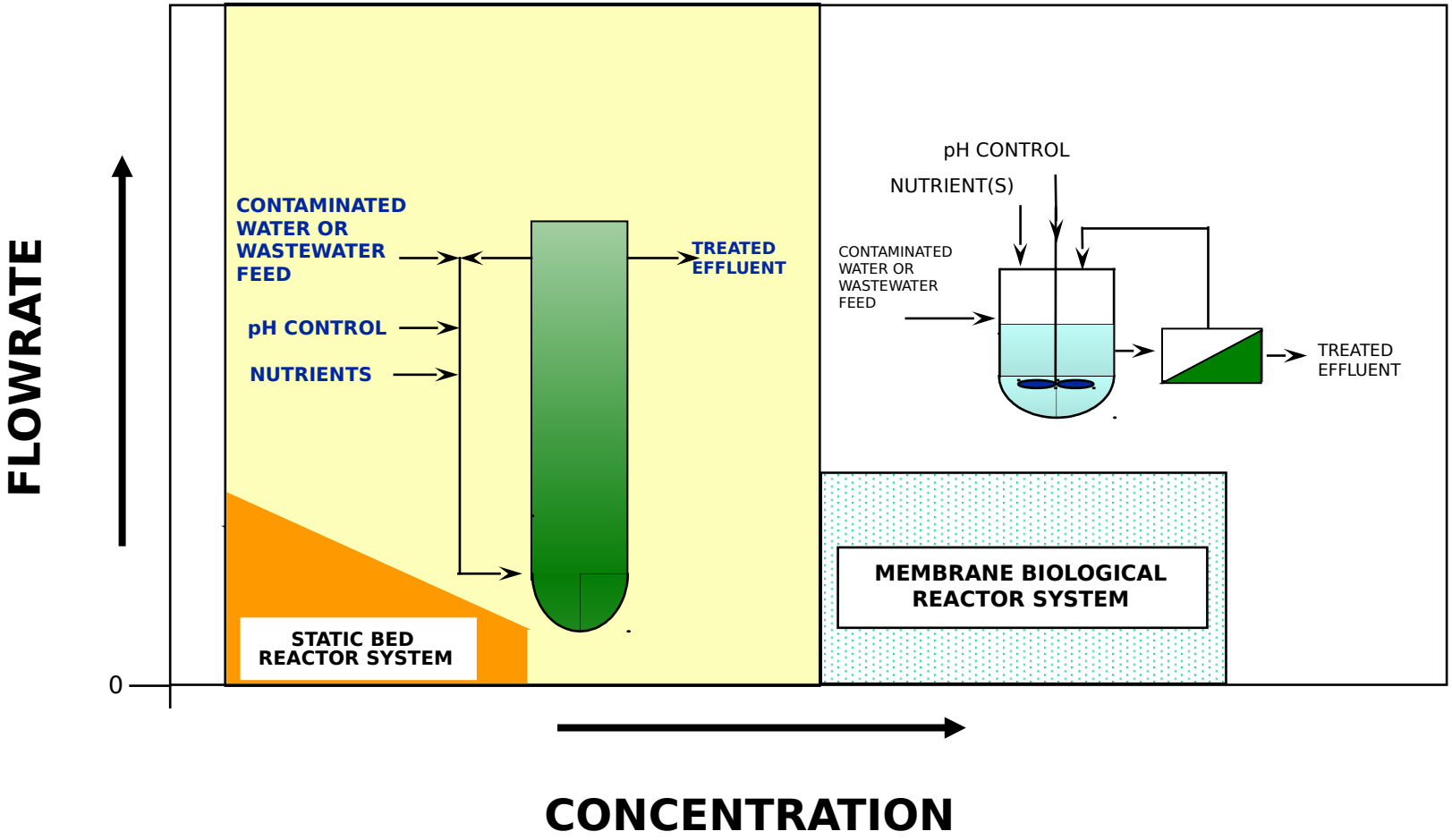
# Bioreactor System Options for Treatment of Perchlorate



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# ıary Treatment Technology: Ion Exchange

- **Basic premise: capture of contaminant anions on positively charged exchange resins**
- **Development scale: both pilot- and full-scale implementation**
- **Advantages:**
  - Currently available
  - Fast reaction and simple operation
  - Can be operated at high flow rate
  - Regulator approved – drinking water applications
- **Disadvantages:**
  - Less cost effective
  - Generates perchlorate-rich waste brine requiring treatment and disposal – can be minimized
  - Contaminated resins require replacement, disposal
  - Competitive uptake by other anions

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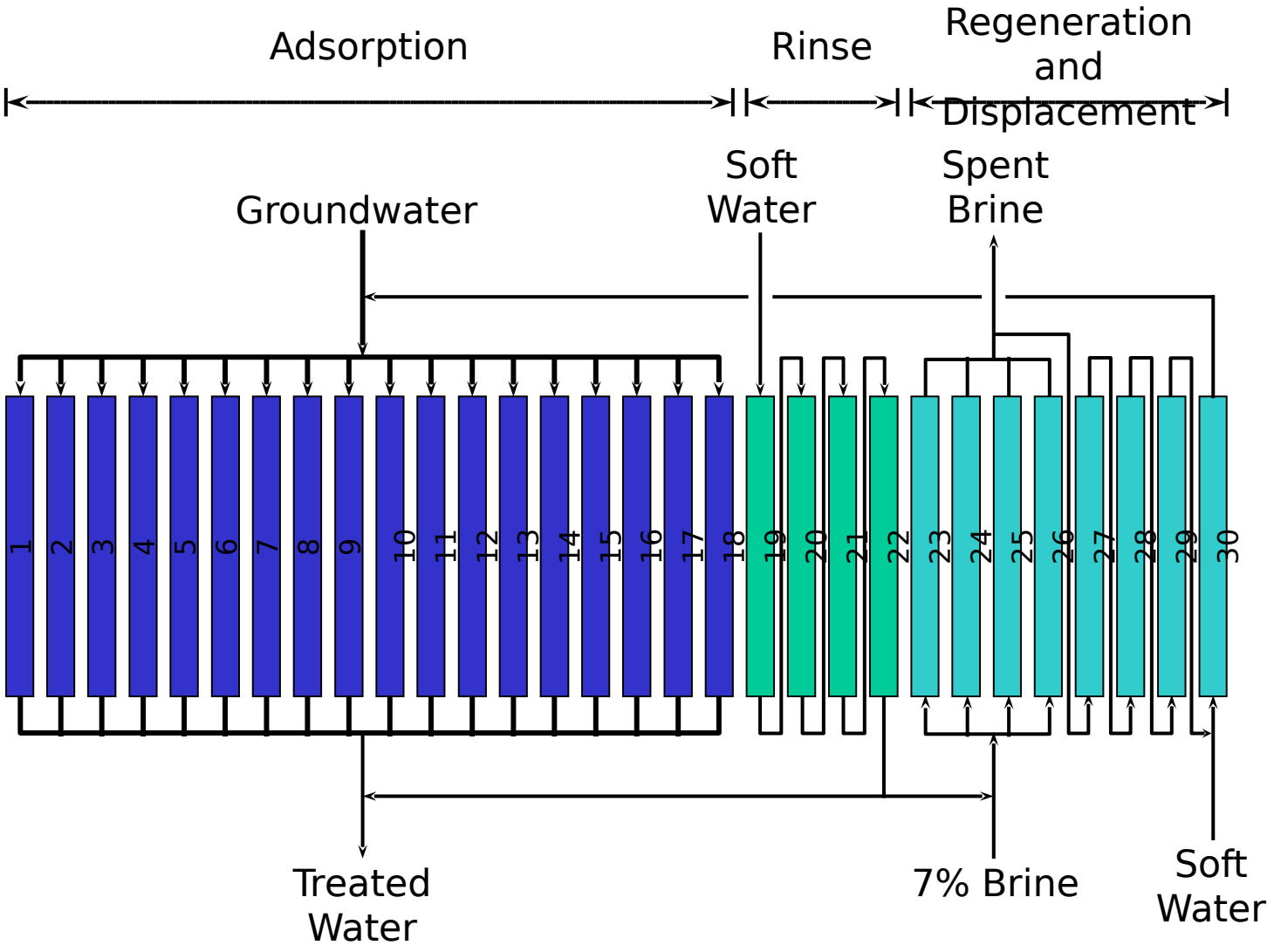
# Ion Exchange Removal of Perchlorate in Groundwater



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# A Variation: Selective Ion Exchange

- **Basic premise: selective capture of perchlorate ion on positively charged exchange resins**
- **Development scale: pilot-scale implementation**
- **Advantages:**
  - Resin selectivity reduces competitive uptake by other anions – less brine generated
  - Low cost brine destruction, resin regeneration process - less frequent replacement and disposal
  - More cost effective
- **Disadvantages:**
  - Still generates contaminated resins, perchlorate brine requiring replacement and disposal
  - Pilot-scale demonstration – technology not approved by regulators

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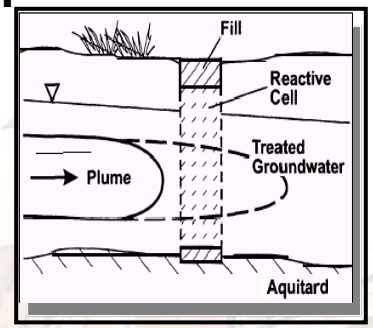
# Emerging Technology: In Situ Bioremediation

- **Basic premise: biological destruction of perchlorate in subsurface**
- **Development scale: pilot scale demonstrations**
- **Advantages:**
  - *In situ* – pump & treat not required, minimizes above ground structures
  - Abundance of naturally occurring microorganisms
  - Can treat source contribution zones
- **Disadvantages:**
  - Drilling required to deliver carbon source
  - Depth to groundwater, pH, $O_2$ content impact effectiveness
  - Aquifer characteristics may result in non-uniform treatment pattern
  - Free movement in groundwater may impact downstream users
  - Non-drinking water applications

# Emerging Technology: Permeable Reactive Barrier

- **Basic premise: biologically active barrier installed in path of groundwater**
- **Development scale: full-scale implementation**
- **Advantages:**
  - Short-term application
  - Pump-and-treat not required - passive *in situ* remediation method
  - Minimal impact on groundwater flow pattern
- **Disadvantages:**
  - Substantial site work required – excavation
  - Depth to groundwater limiting factor
  - Potential clogging by biological, chemical precipitates
  - Does not treat plume down gradient of barrier
  - Abnormal precipitation patterns reduce effectiveness – excessive precipitation can overwhelm barrier, draught can dessicate biologically active organisms
  - Not for drinking water applications



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# Emerging Technology: Soil Composting

- **Basic premise: anaerobic biological degradation of perchlorate - composting**
- **Development scale: field-scale *in situ* and *ex situ* implementation**
- **Advantages:**
  - Short-term technology can treat soil hot spots, source contribution zones
  - May be more cost effective than conventional “dig, haul, treat” approaches
- **Disadvantages:**
  - *Ex situ* requires excavation and environmental controls
  - Static, non-mixing *in situ* may result in non-uniform treatment
  - Effective appears limited to within 18 – 24 inches of surface
  - Potential downstream contamination from *in situ* application

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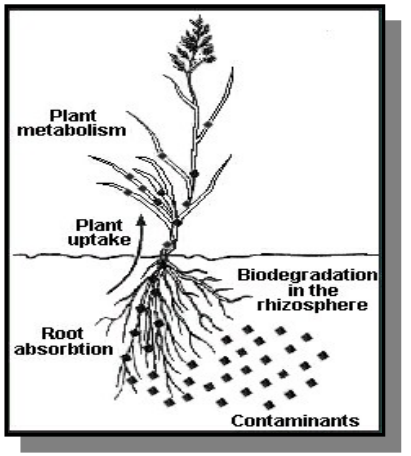
# Emerging Technology: Phytoremediation

- **Basic premise: natural plant processes, root system microorganisms remove, contain, or degrade perchlorate**
- **Development scale: laboratory-, bench-scale implementation**
- **Advantages:**
  - Can treat soil hot spots, source contribution zones and groundwater
  - May be more cost effective than conventional “dig, haul, treat” approaches
  - Passive, aesthetically pleasing
- **Disadvantages:**
  - Depth limits – contaminant must be within reach of plant system
  - Not a short-term option – effective over numerous growing seasons
  - Regulator familiarity and acceptance



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# DOD Perchlorate tment Technology Workgroup

- **Purpose:**
  - **Provide consistent and coordinated approach to treatment technology development and deployment (TTDD)**
  - **Develop and advocate vision of success for TTDD efforts**
  - **Develop coordinated DoD representation to:**
    - **Interstate Technology and Regulatory Cooperation (ITRC)**
    - **Federal Remediation Technologies Roundtable (FRTR)**
    - **SERP/ESTCP**
  - **Keep Service headquarters updated on technology status**
  - **Serve as information clearing house for DOD**
  - **Services: USA, USN, USAF, and other respective service centers**
  - **DUSD(I&E)**

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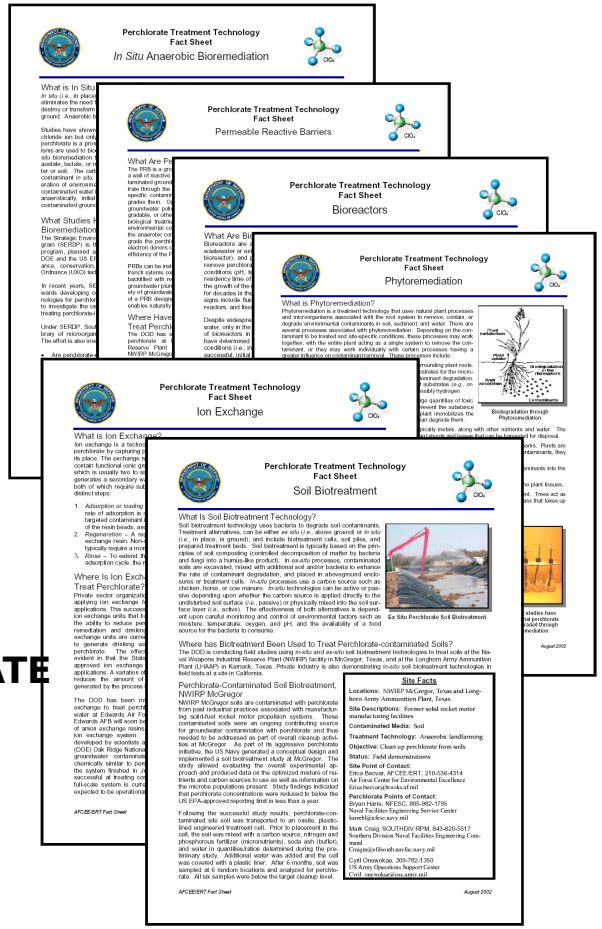
# For More Information on Perchlorate

- **Sample available links:**
  - **www.serdp.org**
  - **www.estcp.org**
  - **www.afcee.brooks.af.mil**
  - **www.denix.osd.mil/denix/Public/Library/Water/Perchlorate/perchlorate.html**
  - **www.epa.gov/ogwdw000/ccl/perchlor/perchlo.html**
  - **www.dhs.cahwnet.gov/ps/ddwem/chemicals/perchl/perchlindex.htm**
  - **www.adeq.state.az.us/environ/water/dw/fact.html**
  - **tera.org/Perchlorate/welcome.htm**
  - **www.gwrtac.org/html/tech_status.html#PERCHLORATE**
  - **www.epa.gov/safewater/ccl/perchlor/r9699fac.pdf**



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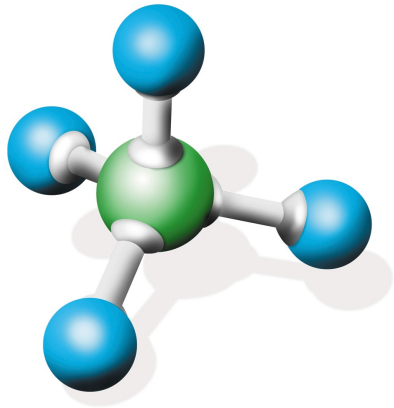
# Looking to the Future

- **PROGNOSIS: Ramp-up of sampling, cleanup activities; potential operational aspects, beginning in FY03**
- **NEEDS:**
  - **Ensure credible science leads to credible cleanup standards (federal and state level)**
  - **Address/develop sampling policy**
  - **Identify future funding sources**
  - **Engage operational community**
  - **Conduct risk/benefit analysis**
  - **Optimize/develop cost-effective treatment te**
  - **Tri-Service & OSD Principles and Practice Published Text**



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